# THE EQUILIBRIUM BETWEEN CARBON MONOXIDE, CARBON DIOXIDE, SULPHUR DIOXIDE, AND FREE SULPHUR

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The value of a study of the equilibrium between CO, CO_2, SO_2, and S_2 lies not in the reaction itself, important as this undoubtedly is both to the scientific and technical worlds, but rather in the fact that from such a study the free energy of sulphur dioxide, a quantity indispensable to a proper study of the chemistry of the sulphur compounds, may be directly obtained. That such an investigation has not heretofore been completed may be ascribed to the many difficulties which appear at the outset to block the way. The complex subsidiary reactions taking place at comparatively low temperatures are the source of many of these and would seem to have deterred Lewis and Lacey[1] from continuing their investigations in this direction. These reactions may be thus summarized:

$$CO + S \rightleftharpoons COS$$
$$2\,COS \rightleftharpoons CO_2 + CS_2$$
$$CS_2 \rightleftharpoons CS + S$$
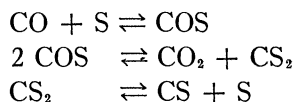
They rendered the ordinary stream methods of investigation useless since by these methods samples could not be obtained which had not reacted after leaving the equilibrium chamber. A semi-stream method devised by the writer obviated this difficulty and samples so obtained from equilibrium mixtures at 1263° abs. showed no evidence of any such reaction taking place. Since the velocities of these reactions greatly exceed that of the main reaction, which goes according to the equation:

$$CO + \tfrac{1}{2} SO_2 \rightleftharpoons CO_2 + \tfrac{1}{4} S_2,$$
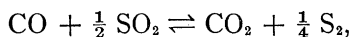
the absence of the products of the former clearly indicated that by this method cooling effects had been eliminated. Details of the method will be given in the final paper. By it a given gas mixture may be heated for a given time at a given temperature and a correct sample of the same then obtained for analysis. It has also the added merit that if the temperature be properly varied the equilibrium can be approached from either side.

A few of the results obtained in this way are presented in the following tables, K being defined by the equation:

$$K = \frac{P_{CO_2}^{\frac{1}{2}} \cdot P_{S_2}^{\frac{1}{4}}}{P_{CO} \cdot P_{SO_2}^{\frac{1}{2}}}$$

All of these with the exception of the measurements at 1458 were obtained from experiments in which platinum was present as a contact mass and the variations are probably due to analytical errors. The two measurements at 1458 were obtained from experiments in which a bare porcelain tube was used as a container and it is unlikely that equilibrium was reached in either case. An average of these two probably will be very near the correct value.

From these results the thermodynamical constant I for this reaction may be calculated by means of the equation:[2]

$$- RT \ln K = \Delta H_0 - \Delta \Gamma\, T \ln T - \tfrac{1}{2}\Delta \Gamma_1 T^2 - \tfrac{1}{6}\Delta \Gamma_2 T^3 + IT \qquad (1)$$

The additional data necessary has been well summarized by Lewis[3] and his co-workers with the exception of the specific heat of S_2 and and the value of ΔH_0 for the reaction $S_R + O_2 = SO_2$. The assumption that the former is the same as that of oxygen leads to the equation for the increase in heat capacity for the main reaction:

$$\Delta \Gamma = - (1.375 - 0.0028\, T + 0.000\,000\,93\, T^2)$$

The further assumption that Berthelot's[4, 5] value of 69400 cal. for the heat of formation of sulphur dioxide from its elements at room temperatures gives for the reaction

$$\tfrac{1}{2}(S_R + O_2 = SO_2) \qquad \Delta H_0 = - 34\,195 \text{ cal.}$$

and for the main reaction

$$CO + \tfrac{1}{2}\, SO_2 = CO_2 + \tfrac{1}{4}\, S_2 \qquad \Delta H_0 = - 25\,915 \text{ cal.}$$

Substituting these values in equation (1) we have

$$- RT \ln K = - 25\,915 + 1.375\, T \ln T - 0.0014 T^2 + 0.000\,000\,155 T^3 + IT$$

In table 3 will be found the values of I calculated by means of this equation from the results found in tables 1 and 2.

<div align="center">

TABLE 1

EQUILIBRIUM APPROACHED FROM THE CO-SO$_2$ SIDE

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TEMPERATURES		
Absolute	Centigrade	Log K
1271	998	1.79
1273	1000	1.73
1273	1000	1.77
1458	1185	1.13
1463	1190	1.19

TABLE 2

EQUILIBRIUM APPROACHED FROM THE CO_2-S_2 SIDE

TEMPERATURES		
Absolute	Centigrade	Log K
1277	1004	1.78
1458	1185	1.27
1463	1190	1.18

TABLE 3

TEMPERATURE	
Absolute	I CALCULATED
1271	3.88
1273	4.12
1273	3.94
1277	3.85
1458	3.97
1463	3.96
1463	4.00
Average value =	3.96

The agreement speaks not only for the results themselves, but justifies the assumption of $-$ 34195 cal. for ΔH_0 for the reaction, $\frac{1}{2}$ ($S_R + O_2$ $= SO_2$) and indicates the correctness of Berthelot's value for the heat of formation of sulphur dioxide. The free energy equations for the two reactions.

$$CO + \tfrac{1}{2} SO_2 === CO_2 + \tfrac{1}{4} S_2 \text{ and}$$
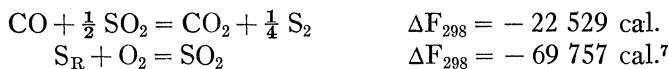$$S_R + O_2 === SO_2$$
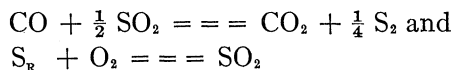
may now safely be written.

The former will be

$$\Delta F_0 = -25\,915 + 1.375\,T \ln T - 0.0014T^2 + 0.000000155T^3 + 3.96T$$

and the latter

$$\Delta F_0 = -68\,391 + 3.62T \ln T - 0.0007\,T^2 + 0.000\,000\,317\,T^3 - 25.03T$$

Under standard conditions, therefore,

$$CO + \tfrac{1}{2} SO_2 = CO_2 + \tfrac{1}{4} S_2 \qquad \Delta F_{298} = -22\,529 \text{ cal.}$$
$$S_R + O_2 = SO_2 \qquad \Delta F_{298} = -69\,757 \text{ cal.}[7]$$

The final paper will appear in the *Journal of the American Chemical Society*.

[1] Lewis, G. N. and Lacey N. *J. Amer. Chem. Soc., Easton, Pa.*, **37**, 1915, (1976)

[2] Lewis, G. N. *Ibid.*, **35**, 1913, (1).

[3] Lewis, G. N. and Randall, M. *Ibid.*, **34**, 1912; (1128), **36**, 1914, (2468); **37**, 1915, (465).

[4] *Ann. chim. phys., Paris*, (Ser. 5), **22**, 1881, (428).

[5] Berthelot's average value of 69260 includes results obtained from experiments in which the sulfur dioxide was determined by means of an alkaline solution. This procedure prob-

ably led to too low results and it is significant that those so obtained were lower than those obtained when iodometric methods were used.   See 'The Iodometric Determination of Sulfur Dioxide and the Sulfites,' J. B. Ferguson, *J. Amer. Chem. Soc., Easton, Pa.,* **39,** 1917, (364).

   [6] Thomsen's value is 71080.   (Thomsen, *Thermische Untersuchungen,* **2,** p. 251)

   [7] This value agrees with that derived from some preliminary investigations by M. Randall on sulfur and water (*Thesis, Mass. Inst. Tech., Boston,* 1912) and also with that obtained by Lewis and Bichowsky in a more complete investigation carried out at higher temperatures (private communication).

PHYSIOLOGICAL EFFECT ON GROWTH AND REPRODUCTION OF RATIONS BALANCED FROM RESTRICTED SOURCES

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Our early work[1] on the nutrition of herbivora with restricted rations demonstrated clearly the inadequacy of the accepted theory as to what constitutes a balanced or complete ration.   Up to that time total protein—without reference to quality—energy, and ash materials were considered the essentials of a ration.   The latter, however, occupied no position in the mathematical expression of the standards developed. The standards have been stated only in terms of total digestible protein and energy.   It is, however, probably true that in a practical sense, and with the generally accepted knowledge of the quality of materials accumulated from a long and varied experience, that such standards have had and will continue to have very great value; but their limitations are also made evident by this earlier work and are emphasized by what we have since done.   Within the past few years our knowledge[2] of the essentials of a ration have expanded and today we would consider a ration complete and efficient only when it contained protein of adequate quantity and quality, adequate energy, ash materials in proper quantity and proportion and two factors of unknown constitution (vitamines), designated from this laboratory[3] fat soluble A and water soluble B.

   In addition to the above normal factors there may be introduced with natural food-stuffs the important factor of toxicity.[4]   This can be wholly absent or so mild in its effects as to be entirely obscured when the other essentials of a ration are at an optimum adjustment; or with fair adjustment it may only reveal its effects when the ration is continued over a very long time and the animal involved in the extra strains of reproduction and milk secretion.   This resistance to toxicity